$M_2CuO_2X_2$: Model compounds for the physics of high temperature superconductors

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Motivation

As structural and electronic analogues of undoped high temperature superconductors in the normal electronic state, these insulating compounds serve as models for unraveling the fundamental physics of the normal state from which superconductivity arises.

Introduction

Since first taking initiative using these analogues to investigate the normal state properties of cuprate high temperature superconductors (HTSCs), they have been viewed as model systems for HTSCs and two dimensional (2D) square lattice antiferromagnets (AF).

Similarities with HTSCs lie in the structure (Fig. 1), magnetic spin interactions (Figs. 2, 3, 4, 6), and electronic structure (Fig. 5). Additionally, these materials become superconducting when electronically doped under high pressure.

Advantages over directly studying the HTSCs are stability of structure, strongly ionic apical Cu bonding, electronically insulating character, and the simplicity of a higher symmetry.

Application of materials science techniques to grow large, high quality, single crystals has enabled us to successfully carry out numerous experiments involving complimentary microscopic and macroscopic techniques. Below are some of the highlights illustrating the insight gained into the physics underlying the electronic behavior of the quasi-2D materials and HTSCs using these crystals.

Highlights

Insulating nature measured at higher temperatures and tetragonal structural (Fig. 1) stability proven to at least 10K. This makes them less complicated than the HTSCs which have either electronic / structural transformations or additional interactions.

In-plane AF interactions found to be similar in strength to the HTSCs and they have comparable Néel temperatures (T_N) (Figs. 2, 3). The normally unimportant weak dipolar interactions were calculated to be the determining factor in the in-plane AFM ordering direction.

A second stacking sequence of the AF planes was discovered in $Ca_2CuO_2Cl_2$ (Figs. 2, 3). Experiments and model calculations led to the proposed models. The very weak, sequence-determining, inter-planar interactions are still incompletely understood. High-order quantum-chemical effects are being poised as explanations.

The field dependence of T_N was discovered (Fig. 4) and explained using a magnetic field induced, Ising-like symmetry model.

Probing electronic excitations with angle resolved photoemission (ARPES), electron energy loss, and two magnon Raman scattering techniques have identified unexpected electronic structure lying between the valence and Fermi levels (E_F) (Fig. 5). Believed to be either the "bands" or closely related to the bands in which superconductivity occurs. Normal state theories are being tested against the spectra as are the results of the more complicated HTSCs.

A crossover in the magnetic spin behavior was discovered where the spins begin to become limited to 2D far above T_N, dispelling beliefs that the lowered spin dimensionality and 3D ordering occurred at essentially the same temperature (Fig. 6).

A new technique was developed to dope $Sr_2CuO_2Cl_2$ with fluorine for ^{19}F NMR and photoemission analyses. The low temperature technique was used to dope and study the superconducting flux lines in the HTSC $YBa_2Cu_4O_8$.

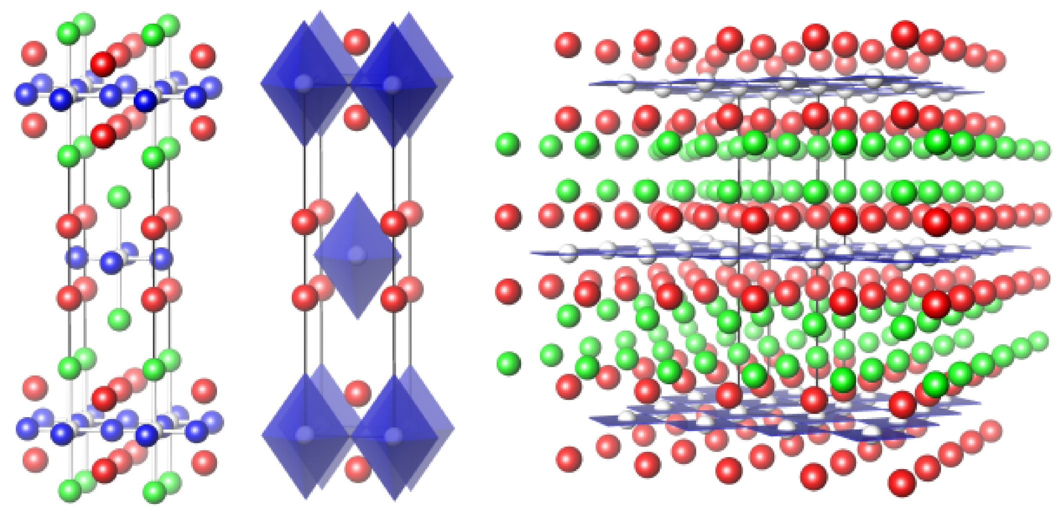
Muon spin rotation (μ^+SR) studies found muons to locate in the CuO_2 plane, complimenting local Cu-moment measurements on HTSCs where the muons reside above the plane.

Current Research

Intriguing experimental results at moderately low temperatures are being investigated. A transition <100K has been seen in the static and AC susceptibility, ^{35}Cl NMR, heat capacity, and μ^+SR data. Having ruled out the classical explanation of these subtle observations, a quantum physical origin of this macroscopic phenomena is currently sought.

The interpretation of the electronic spectra is currently the most important aspect, of the study of $Ca_2CuO_2Cl_2$ and $Sr_2CuO_2Cl_2$. Several collaborative spectroscopic studies focusing on the electronic levels, just below and above E_F, in these insulators and several HTSC compounds are being carried out in hopes of finding further insights into the roots of superconductivity.

Our understanding of the physics of magnetic and electronic interactions are being pushed to higher orders using experimental results from these materials. Normally strong interactions cancel due to the high symmetry, forcing us to reexamine old approximations and assumptions. One example is the differences in stacking of the AF planes in $Ca_2CuO_2Cl_2$ and $Sr_2CuO_2Cl_2$.



I4/mmm	Lattice Parameters
La_2CuO_4	a=3.79Å, c=13.2Å
$Ca_2CuO_2Cl_2$	a=3.87Å, c=15.1Å
$Sr_2CuO_2Cl_2$	a=3.97Å, c=15.6Å

FIGURE 1. Views of the $M_2CuO_2X_2$ tetragonal crystallographic structure. Left to right the panels emphasize the **Cu bonding**, the octahedral **Cu coordination**, and the isolated square planar **CuO_2 sheets** wherein superconductivity lies. La_2CuO_4 shown without orthorhombic distortion.

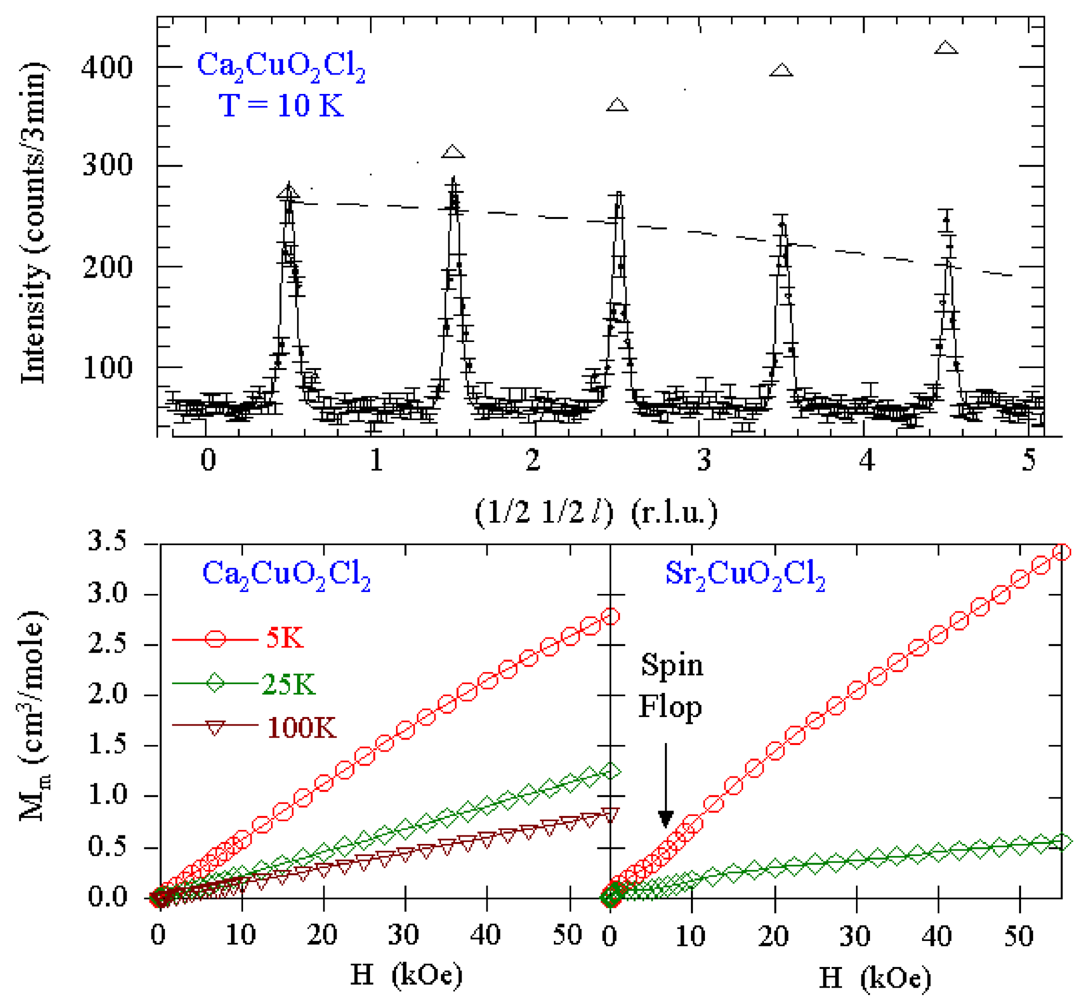


FIGURE 3. Single crystal magnetic neutron diffraction from $Ca_2CuO_2Cl_2$ revealing an unexpected doubling of the magnetic unit cell along the c-axis. Isothermal magnetization showing the absence of the metamagnetic **spin flop** transition in $Ca_2CuO_2Cl_2$ which is evident in $Sr_2CuO_2Cl_2$ below 1 Tesla.

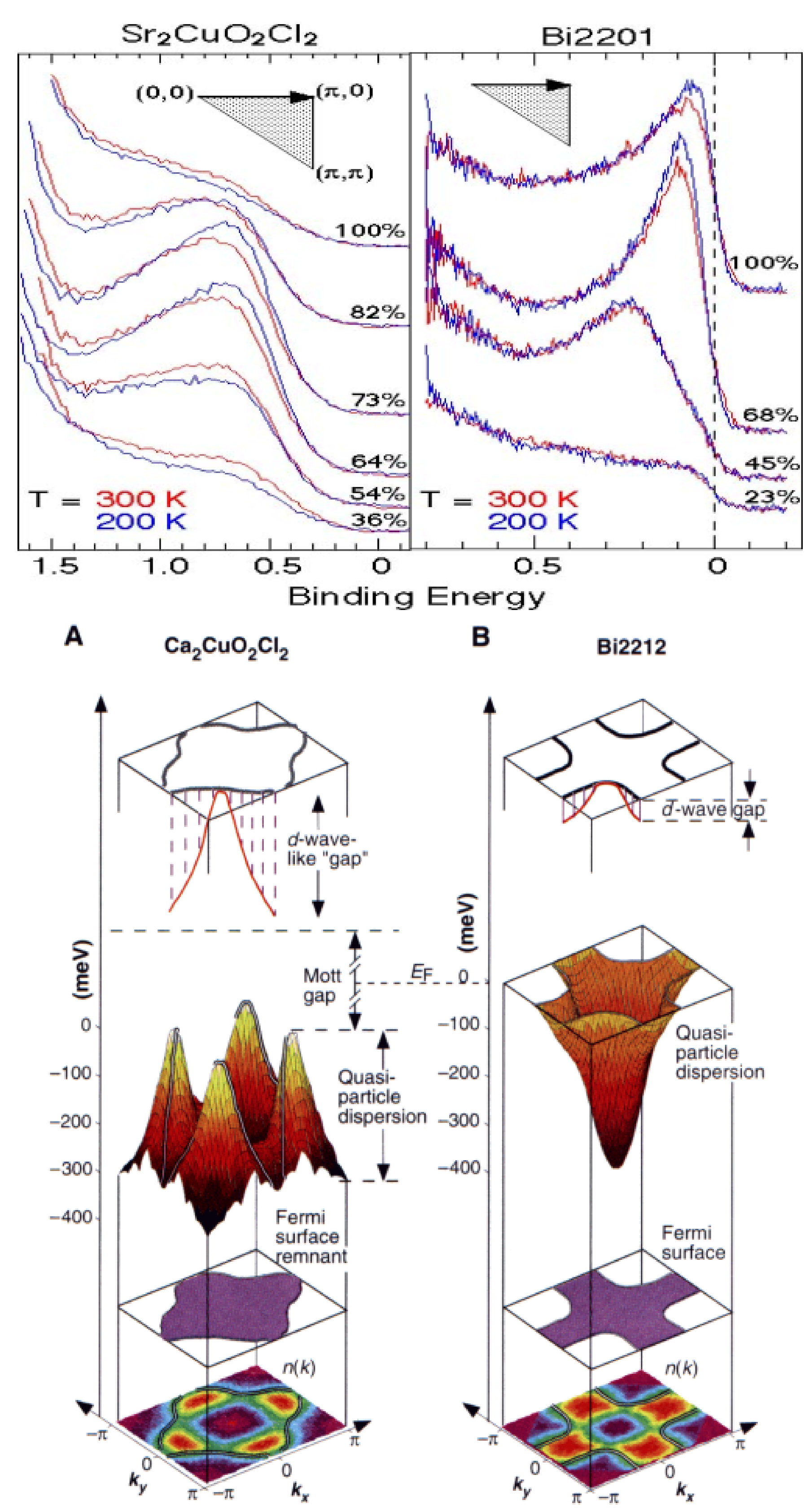


FIGURE 5. ARPES comparison of $M_2CuO_2X_2$ single crystals with results from BSSCO High Temperature Superconductors. Upper panels compare temperature and angular dependence of the low energy excitations. Lower panel compares symmetry of quasiparticle band with the Fermi surface of BSCCO.

Néel Temperatures	
La_2CuO_4	320K
$Sr_2CuO_2Cl_2$	260K
$Ca_2CuO_2Cl_2$	250K

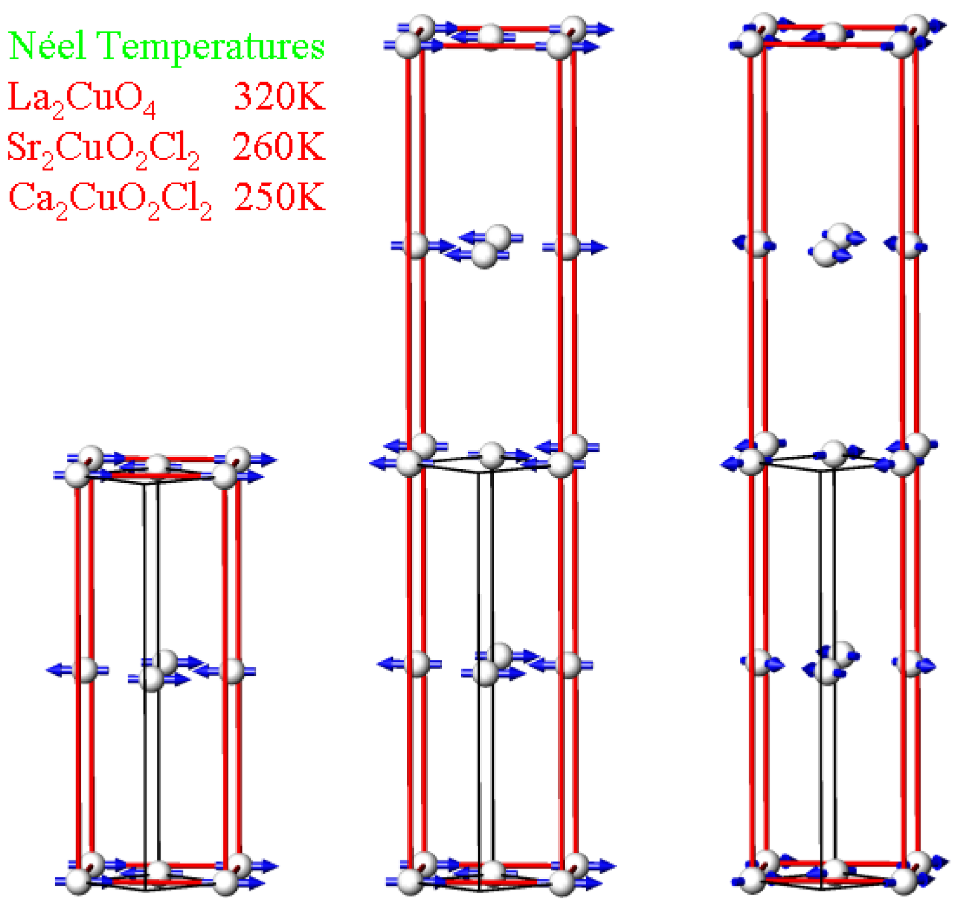


FIGURE 2. **Antiferromagnetic** ordering in $M_2CuO_2X_2$. Left panel shows the √2x√2 magnetic unit cell of La_2CuO_4 (without structural distortion) and $Sr_2CuO_2Cl_2$. Middle and right panels show our proposed √2x√2x2 **doubled** magnetic unit cells of $Ca_2CuO_2Cl_2$. Arrows represent a single magnetic spin on each Cu atom. Non-magnetic atoms have been removed for clarity. Crystallographic unit cells are shown in black.

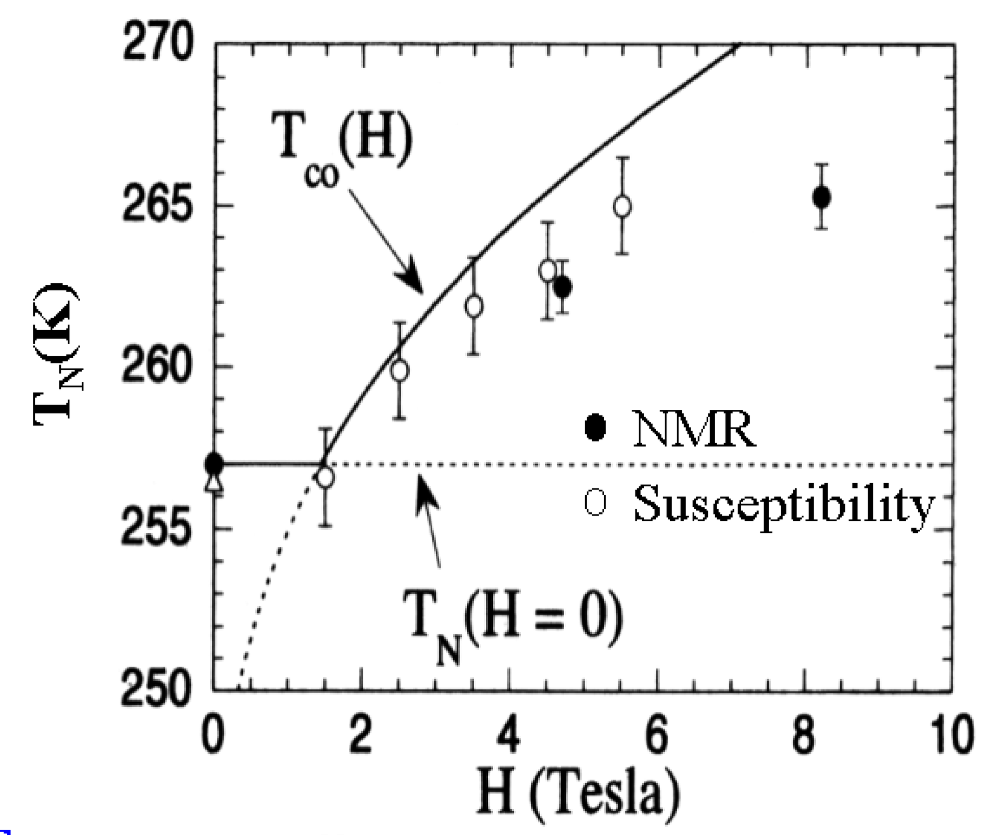


FIGURE 4: χ and ^{35}Cl NMR results for $Sr_2CuO_2Cl_2$ showing an **increase** in T_N when H is parallel to the CuO_2 planes. Solid and dotted lines represent simple cases for comparison.

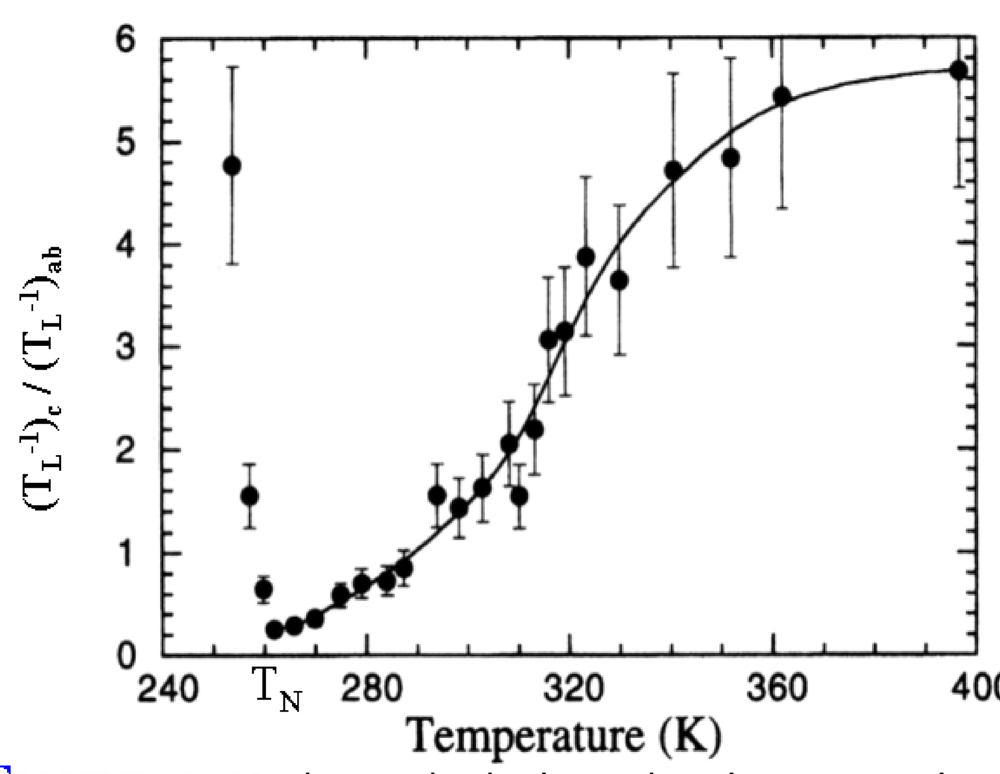


FIGURE 6: Nuclear spin lattice relaxation rate ratio for $Sr_2CuO_2Cl_2$ showing evidence of the **crossover** in the spin dynamics around 350K, from high temperature Heisenberg to XY-like, well above T_N = 260K. Below lies a table listing magnetic spin regimes found in $Sr_2CuO_2Cl_2$.

Magnetic Transitions

States	T(K)	Spin Ordering	Important Interactions	Spin Orientation
PM	>1200	none	none	3D, Paramagnetic
2D AF	1200	2D†	2D	3D, Heisenberg
2D AF	350	2D†	2D	2D, XY-like
3D AF	260	3D	3D	1D, Néel State
3D AF	50	3D	3D	Spins reorient?

†Dynamic, short range ordering.

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